

CLAIMS

1. Coloration process for obtaining on the surface and/or in the interior of fired ceramic material a variation in the resultant colour of iron-based colorant solutions characterised by:
 - 5 (a) adding to the ceramic mix from 1% to 15% by weight with respect to the dry ceramic mix, precipitated silica and/or silica gel having an active surface $S \geq 100 \text{ m}^2/\text{g}$ at the moment of coloration, said active surface S being defined by the formula
$$S = A * Gr, \text{ where:}$$
 - 10 (b) Gr is the particle size fraction comprised between 5 and 60 micron for precipitated silica and between 1 and 60 micron for silica gel, and A is the surface area of the silica expressed in m^2/g measured by the B.E.T. method;
 - 15 (c) applying to the surface of the additive-containing ceramic mix aqueous or organic solutions comprising inorganic salts of Fe(II) and/or Fe (III), or organic derivatives of Fe(II) and/or Fe(III);
 - (d) the variation in the resultant colour being equal to $\Delta E > 6$.
2. Process as claimed in claim 1, characterised by adding to the ceramic mix precipitated silica and/or silica gel in a total quantity between 2% and 10% by weight of dry silica with respect to the dry ceramic mix.
- 20 3. Process as claimed in claim 2, characterised by adding to the ceramic mix precipitated silica and/or silica gel in a total quantity between 3% and 7% by weight of dry silica with respect to the dry ceramic mix.
4. Process for colouring ceramic materials as claimed in claims 1-3, characterised in that step (a) is implemented by adding precipitated silica and/or silica gel to the raw materials or to the slip.
- 25 5. Additive-containing ceramic mix obtained according to step (a) of one or more of claims 1-4.
6. Coloration process according to one or more of claims 1-4, employing at least one additive-containing ceramic mix according to claim 5 in inhomogeneous admixture along with further ceramic mixes.
- 30 7. Inhomogeneous mixture of ceramic mixes comprising at least one additive-containing mix as of claim 5.

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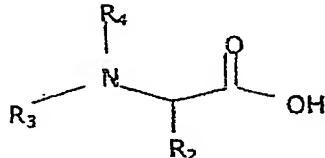
8. Process for colouring ceramic materials as claimed in one or more of claims 1-4 or 6, characterised in that the additive-containing ceramic material as of claim 5 or 7 is treated with aqueous solutions containing from 0.1% to 20% by weight of iron (expressed as elemental Fe) in the form of inorganic salts of Fe(II) and/or Fe (III), or organic derivatives of Fe(II) and/or Fe(III).

9. Process for colouring ceramic materials as claimed in one or more of claims 1-4 or 6 or 8, characterised in that the organic derivatives of Fe(II) and/or Fe(III) are salts and/or complexes with organic compounds chosen from the group acetylacetone; ascorbic acid;

10 carboxylic acids of general formula $R_1\text{-COOH}$ and/or the sodium, potassium or ammonium salt thereof in which R_1 represents hydrogen, a benzene ring or a C1-C9 alkyl or alkenyl group possibly substituted with from 1 to 6 -COOH, -OH, NH_2 and/or -SH groups;

amino acids of general formula

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and/or a sodium, potassium or ammonium salt thereof where

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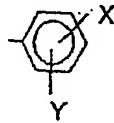


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where R_3 and R_4 can be equal or different among each other and represent hydrogen, a C1-C4 alkyl group possibly substituted with -OH groups,

$-(\text{CH}_2)_n\text{-COOH}$ where $n = 1-3$, $-(\text{CH}_2)_m\text{-NH}_{(2+)}\text{-}(\text{CHR}_5\text{-COOH})_k$ in which $m = 1-6$ and

$k = 1$ or 2 , and where $R_5 = \text{H, CH}_3$,



where $X = \text{H, -CH}_3$ and

$Y = \text{H, -OH}$.

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10. Process for colouring ceramic materials as claimed in one or more of claims 1-4 or 6, 8, 9, characterised in that for colouring the additive-containing ceramic material, an aqueous solution of iron ammonium citrate containing 0.3% to 20% by weight of iron (expressed as elemental Fe) is used.

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11. Process for colouring ceramic materials as claimed in claim 10, characterised in that for colouring the additive-containing ceramic material, an aqueous solution of iron ammonium citrate containing from 1% to 20% by weight of iron (expressed as elemental Fe) is used.
- 5 12. Process for colouring ceramic materials as claimed in one or more of claims 1-4 or 6 or 8, characterised in that the colorant solutions are aqueous solutions containing iron (II) ammonium sulfate, iron (II) sulfate, iron (II) chloride, iron (II) perchlorate, potassium hexacyanoferrate (II), potassium hexacyanoferrate (III) ammonium hexacyanoferrate (II).
- 10 13. Process for colouring ceramic materials as claimed in one or more of claims 1-4 or 6, 8-12, characterised in that the colorant solutions containing iron in the form of inorganic salts of Fe(II) and/or Fe (III), or organic derivatives of Fe(II) and/or Fe(III) also comprise inorganic salts and/or organic derivatives of metals chosen from the group: Co, Ni, Cr, Ru, Au, Mn, Ti, Zn, Zr, Sb, V, W, Pd or their mixtures.
- 15 14. Process for colouring ceramic materials as claimed in claim 13, characterised in that the colorant solutions contain 0.1-18.2% by weight of iron (expressed as elemental Fe), with a maximum cation concentration of 20%, and have a Fe/Me weight ratio between 15/1 and 1/5, where in the case of several metals different from Fe, Me means the sum by weight of the concentration of the different metals.
- 20 15. Process for colouring ceramic materials as claimed in claim 14, characterised in that the colorant solutions contain 0.3-18.2% by weight of iron (expressed as elemental Fe), with a maximum cation concentration of 19.5%, and have a Fe/Me weight ratio between 13.9/1 and 1/5, where in the case of several metals different from Fe, Me means the sum by weight of the concentration of the different metals.
- 25 16. Process for colouring ceramic materials as claimed in one or more of claims 1-4 or 6, 8-15, characterised by the following operative steps:
 - (a) adding precipitated silica and/or silica gel to the ceramic mix to be moulded in a quantity between 1% and 15%, preferably between 2% and 10%, more preferably between 3% and 7% by weight of dry silica with respect to the dry ceramic mix;
 - 30 (b) moulding the ceramic mix;
 - (c) drying the moulded ceramic material;
 - (d) treating the ceramic material derived from the preceding step with at least

2g/m² of colorant solution;

(e) drying the ceramic material derived from the preceding step;

(f) firing the ceramic material.

17. Process for colouring ceramic materials as claimed in claim 16, characterised in that between step (c) and step (d), one or more intermediate steps (c') of pre-treating the dried material are carried out, using water or aqueous solutions of mono- or poly-carboxylic acids or of their salts.

18. Process for colouring ceramic materials as claimed in claim 16 or 17, characterised in that between step (d) and step (e), one or more intermediate steps (d') of post-treating the material previously treated with colorant solution are carried out, using water or aqueous solutions of mono- or poly-carboxylic acids or of their salts.

19. Process for colouring ceramic materials as claimed in claim 16 or 17, characterised in that between step (d) and step (e), one or more intermediate steps (d') of post-treating the material previously treated with colorant solution are carried out, using aqueous solutions of inorganic salts.

20. Process for colouring ceramic materials as claimed in claims 18 and 19 wherein step (d') is carried out post-treating with aqueous solutions comprising mono- or poly-carboxylic acids or their salts, as well as inorganic salts.

21. Totally or partially decorated ceramic material obtainable in accordance with one or more of the process variants described in claims 1-4 or 6, 8-20.

22. Decorated ceramic material as claimed in claim 21, the surface of which has been subjected after firing to satinizing, smoothing, polishing or lapping.

23. Decorated ceramic material as claimed in claim 22 which is of porcelain stoneware.